JOC The Journal of Organic Chemistry

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# Noncovalent Control of Absorption and Fluorescence Spectra

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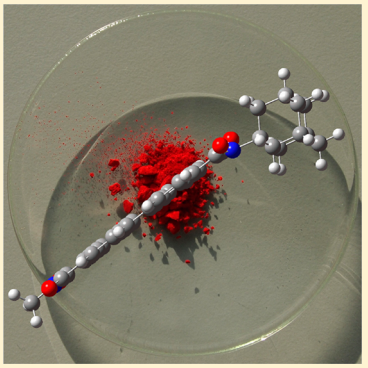
Supporting Information

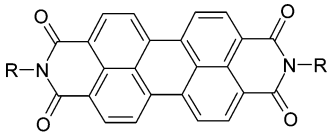
**ABSTRACT:** Perylene dyes with N-*tert*-alkyl substituents were prepared in which noncovalent interactions of the crowded substituent cause a variation of the geometry of the core and induce hypsochromic shifts in absorption and fluorescence. The interpretation of the shifts was supported by means of DFT calculations and an X-ray crystal structure analysis.



## INTRODUCTION

Noncovalent interactions are of importance for many fields in chemistry in which research is focused on the control of chemical reactivity.[1] However, the potential of noncovalent interactions for controlling the properties of conjugated systems has received much less attention. The geometry of delocalized structures determines many properties such as the energetic distance between the HOMO and LUMO, where noncovalent interactions by attached groups (R) may be used to modulate properties; such effects are studied here.

**Chart 1. Perylenetetracarboxylic Bisimides 1**



**1**

## RESULTS AND DISCUSSION

We used the perylene-3,4:9,10-tetracarboxylic bisimides[2,3] **1** as the basic elements of the conjugated structure because of their chemical and photochemical stability and high fluorescence quantum yields. The experimentally found invariance of the UV/vis absorption and fluorescence spectra with regard to solvent effects[4] and the substituent R is an important feature in choosing perylene bisimide dyes for various applications. The most bathochromic UV/vis absorption is dominated by the electronic transition between the HOMO and LUMO, where there are nodes in the wave function at the nitrogen atoms[5] in these orbitals. As a consequence, N substituents are ideal for controlling physical properties without influencing the chromophore. Moreover, the attachment of saturated carbon atoms to the nitrogen atoms means an efficient additional decoupling of the chromophore from further atoms of the substituents.

A long-chain *sec*-alkyl substituent (swallowtail substituent) such as the 1-hexylheptyl group in **1a** was attached to the nitrogen atoms to improve solubility.[6] The UV/vis spectra of such compounds are invariant with regard to the chain length and even removal of one branch each to give primary alkyl groups such as the hexyl group in **1g**, which has very little influence on the spectra (see Figure 1, dotted and dashed lines; see the inserts for enlargements of the absorption and fluorescence spectra).

However, little is known about **1** with tertiary substituents, for which no special spectral properties were reported. Synthesis by the condensation of *tert*-alkylamines with perylene-3,4:9,10-tetracarboxylic bisanhydride proved to be difficult because standard syntheses with dilute solutions in quinoline or imidazole were not successful. Either an addition of DCC was necessary,[7] forming problematic byproducts that were difficult to remove, or a reported synthesis[8] in refluxing DMF could not be reproduced to give pure material. We found that a condensation in a large excess of pure amine gave surprisingly good results. We started such syntheses with the anhydride−carboximide **2**, in which the solubilizing 1-hexylheptyl substituent simplifies syntheses, purification, and spectroscopic investigations and lowers the tendency for aggregation. The condensation of **2** with neat molten 1-aminoadamantane allowed the preparation of **1c** in 54% yield. The synthesis of the more simple **1b** was made difficult by the

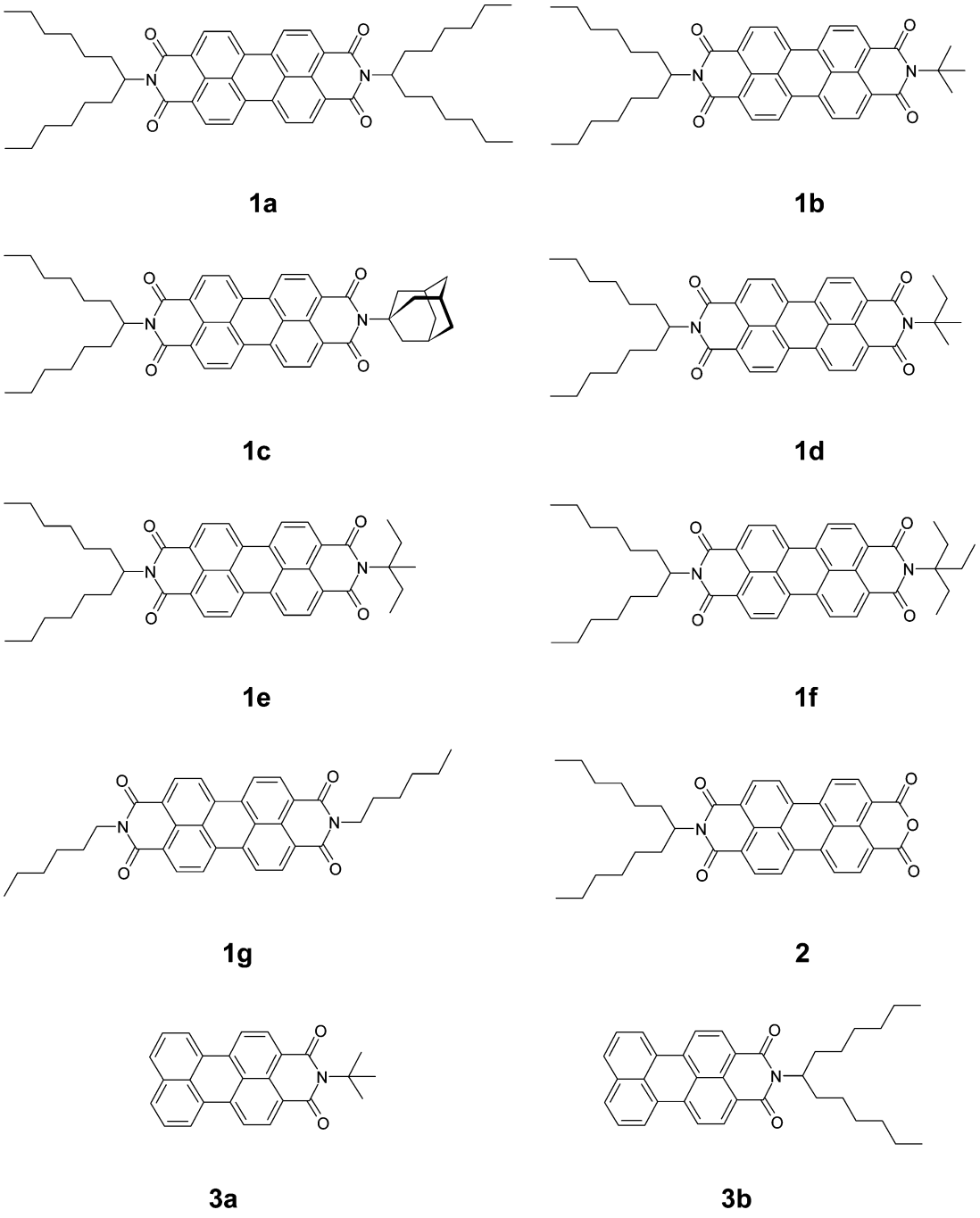
**Received:** March 16, 2012
**Published:** June 28, 2012





dx.doi.org/10.1021/jo300540h | J. Org. Chem. 2012, 77, 5965−5970

**Chart 2. Perylene Derivatives**




low boiling point of *tert*-butylamine. Synthesis became successful with the addition of a small amount of imidazole as an unproblematic high-boiling additive. This forms a difficult balance between boiling-point elevation and dilution. A **2**/*tert*-butylamine/imidazole molar ratio of 1/10/10 is a good compromise for synthesis. We increased the crowding of alkyl groups by the successive replacement of the methyl groups at the tertiary center of **1b** with ethyl groups to give **1d**–**f**; the yields decreased with crowding. Finally, the novel method of condensation was successfully applied to perylene-3,4-dicarboxylic anhydride to give **3a**.

The UV/vis spectra of **1b** were hypsochromically shifted by 4 nm in both absorption and fluorescence (see the continuous lines in Figure 1), as were the spectra of the other *tert*-alkyl derivatives of **1**. The high fluorescence quantum yield of **1** was not affected by these spectral alterations. The same results were found for **3**, where a similar hypsochromic shift was observed for the N-*tert*-alkyl derivative **3a** in comparison to N-*sec*-alkyl derivatives such as **3b** (see Figure 2).

We interpret these results as a consequence of noncovalent interactions of the crowded N substituent with the conjugated system and applied quantum chemical calculations (DFT, B3LYP) for further clarification, where we simplified the long-chain *sec*-alkyl substituent to an isopropyl group in **1h**–**j** (see Chart 3).

We calculated the expected planar geometry for **1i**, in which the methyl groups are symmetrically oriented above and below the aromatic plane and the remaining hydrogen atom is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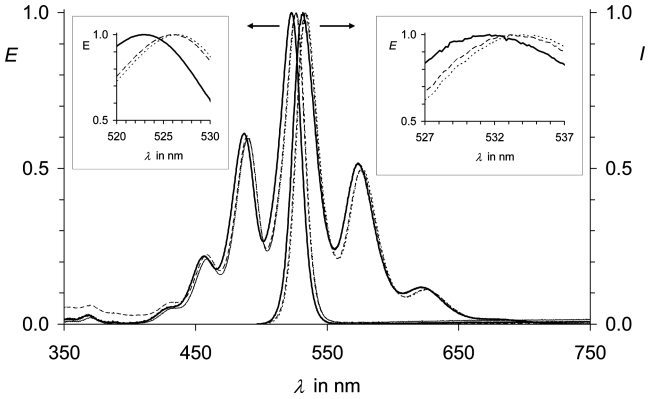



**Figure 1.** UV/vis absorption (left) and fluorescence (right) spectra of perylene dyes in chloroform at 25 °C: (—) **1b**; (···) **1a**; (- - -) **1g**. Insets give enlargements of the absorption (left) and fluorescence spectra (right).

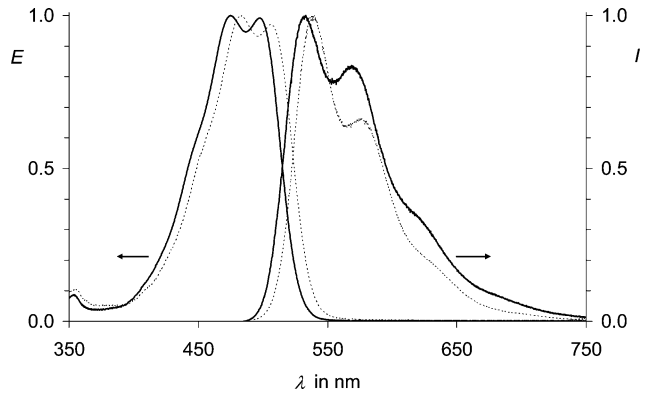



**Figure 2.** UV/vis absorption (left) and fluorescence spectra (right) of **3a** (—) and **3b** (···) in chloroform at 25 °C.

directed toward the neighboring oxygen atom (see Figure 3). The planarity of the system is indicated by a dihedral angle of 0° for $C3_{aryl}–C_{C=O}–N–C_{C–N}$. A very similar geometry with a dihedral angle of 0° was found for the derivative **1h**, with a primary alkyl group. The geometry of **1j** differs in that the *tert*-butyl group is bent out of plane and a dihedral angle of 21° was found; two methyl groups are symmetrically placed at each side and the third methyl is at the other side of the aromatic plane between the carbonyl groups. Both steric interactions and cohesive effects[9] could be responsible for the movement out of plane, where the latter seems to contribute noticeably because the nitrogen atom is placed appreciably more out of plane than the oxygen atoms. The movement out of plane diminishes the conjugation within the chromophore and causes the hypsochromic shift induced by the *tert*-alkyl group. The hypsochromic shift between *prim*- or *sec*-alkyl-substituted and *tert*-alkyl-substituted perylenes is correctly reproduced by the

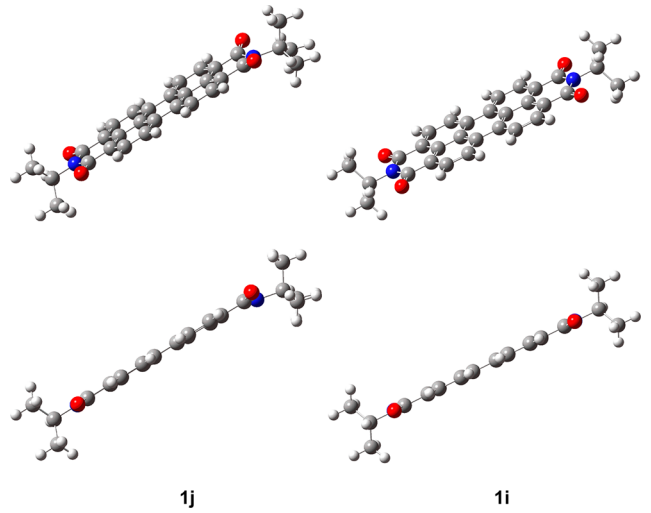



**Figure 3.** Calculated structures (DFT, B3LYP) of **1j** (left) and **1i** (right).

calculations, where an increase of difference between the HOMO and LUMO corresponds to a hypsochromic shift of 3 nm.

Similar results were obtained for perylenedicarboximide, where the *N*-isopropyl derivative was found to be planar with a dihedral angle of 0° ($C3_{aryl}–C_{C=O}–N–C_{C–N}$), whereas 13° was calculated for the bent structure of **3** corresponding to a calculated hypsochromic shift of 3 nm (Figure 4). The bent structure **3** seems to be as similarly stiff as the planar structure with *sec*-alkyl groups because the Stokes shifts are very similar (see Figure 2).

The calculations concerning **3a** were further supported by an X-ray crystal structure analysis, in which a dihedral angle ($C3_{aryl}–C_{C=O}–N–C_{C–N}$) of 19.7° was found for **3a**, whereas a nearly planar structure with a dihedral angle of 4° was reported for the known cyclooctyl derivative[10] (see Figure 5). Some influence of crystal forces has to be taken into account for the X-ray crystal structure analyses.

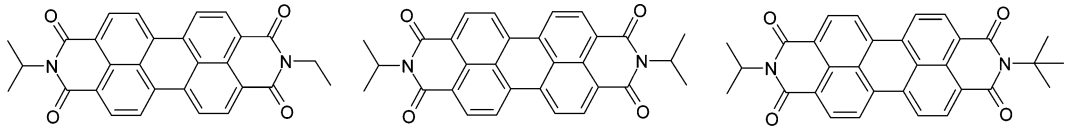
## ■ CONCLUSIONS

The electronic properties of conjugated systems can be influenced by noncovalent interactions and can cause hypsochromic shifts in the UV/vis absorption and fluorescence, such as in **1b–f** and **3a**, respectively. Absorption and fluorescence spectra were simultaneously shifted, and fluorescence quantum yields remain unaffected by such shifts. This method can be applied to a fine-tuning of UV/vis spectra.

## ■ EXPERIMENTAL SECTION

**General Considerations.** All FAB spectra were recorded in 3-nitrobenzyl alcolol as the matrix. The interpretation of NMR signals

**Chart 3. Simplified Perylene Derivatives 1h–j for Quantum Chemical Calculations**





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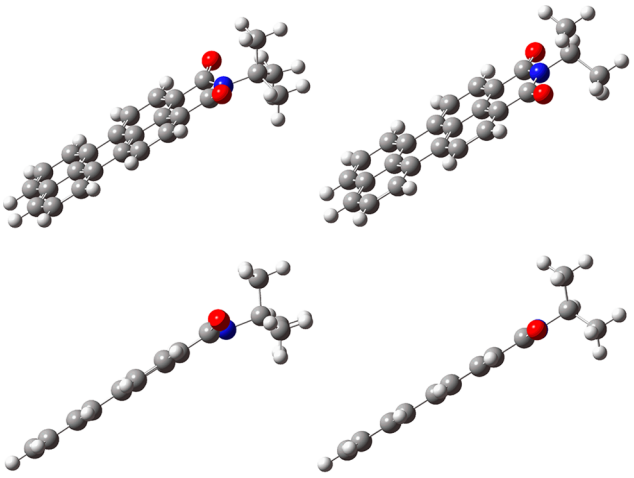
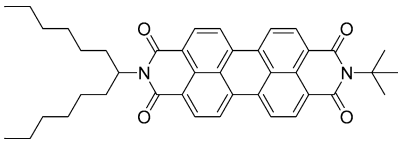



**Figure 4.** Calculated structures (DFT, B3LYP) of **3** (left) and *N*-isopropylperylene-3,4-dicarboximide (right).

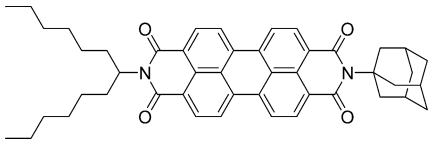
was verified with carbon−proton and proton−proton correlation methods.

**2-*tert*-Butyl-9-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d*′*e*′*f*′]diisoquinoline-1,3,8,10-tetraone (1b).** 9-(1-Hexylheptyl)-2-



benzopyrano[6′,5′,4′:10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10-tetraone (**2**; 50 mg, 87 μmol) was dissolved in imidazole (60 mg, 0.87 mmol) at 150 °C and treated with *tert*-butylamine (64 mg, 0.87 mmol). The mixture was left at 150 °C for 20 min, cooled, treated with $CHCl_3$ (25 mL), and poured into 2 M aqueous HCl (25 mL). The organic phase was collected, washed with distilled water (2 × 25 mL), dried with $Na_2SO_4$, and evaporated in vacuo. The residue was purified by column separation (silica gel 800 × 44 mm, chloroform). Yield: 8 mg (15%), red solid. Mp: >250 °C. $R_f$ value (silica gel, chloroform): 0.50. IR (ATR): $\nu$ 2954.2 (w), 2924.7 (m), 2856.0 (w), 1696.6 (m), 1645.7 (s), 1594.2 (m), 1576.6 (w), 1504.0 (w), 1484.5 (w), 1460.5 (m), 1434.2 (w), 1405.2 (m), 1331.9 (s), 1258.5 (m), 1248.2 (w), 1204.4 (w), 1176.2 (w), 1165.0 (m), 1122.4 (m), 1029.6 (w), 959.2 (w), 847.8 (m), 808.2 (s), 798.6 (w), 772.2 (w), 742.4 (s), 725.5 $cm^{-1}$ (w). $^1H$ NMR (600 MHz, $CDCl_3$, 25 °C): $\delta$ 0.81 (t, $^3J$(H,H) = 6.7 Hz, 6 H, 2 × $CH_3$), 1.17−1.37 (m, 16 H, 8 × $CH_2$), 1.82 (s, 9 H, 3 × $CH_3$), 1.82−1.89 (m, 2 H, $\beta$-$CH_2$), 2.20−2.27 (m, 2 H, $\beta$-$CH_2$), 5.14−5.20 (m, 1 H, C-NH), 8.48−8.69 ppm (m, 8 H, 8 × $CH_{perylene}$). $^{13}C$ NMR (150 MHz, $CDCl_3$, 25 °C): $\delta$ 14.0, 22.5, 26.9, 29.2, 29.8, 31.7, 32.4, 54.7, 61.7, 122.7, 123.0, 125.8, 126.1, 126.5, 128.7, 129.6, 130.4, 133.8, 134.6, 165.1 ppm. UV/vis ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) 456.6 (20 800), 486.8 (50 800), 523.0 nm (80 400). Fluorescence ($CHCl_3$, $\lambda_{exc}$ 487 nm): $\lambda_{max}$ ($I_{rel}$) 531.6 (1.00), 573.4 (0.51), 620.6 nm (0.12). Fluorescence quantum yield ($CHCl_3$, $\lambda_{exc}$ = 487 nm, $E_{487\ nm/1\ cm}$ = 0.0137, reference **1a** with Φ = 1.00): 1.00. MS (DEP/EI): *m*/*z* (%) 628.4 (12) [$M^+$], 572.3 (17), 446.1 (8), 390.1 (100), 345.1 (6). HRMS ($C_{41}H_{44}N_2O_4$): calcd 628.3301 [$M^+$], found 628.3293 [$M^+$], Δ = −0.0008. Anal. Calcd for $C_{41}H_{44}N_2O_4$ (628.3): C, 78.31; H, 7.05; N, 4.46. Found: C, 77.92; H, 6.98; N, 4.44.

**2-(Adamantan-1-yl)-9-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d*′*e*′*f*′]diisoquinoline-1,3,8,10-tetraone (1c).** 1-Ami-



noadamantane (750 mg, 4.97 mmol) was molten and treated with 9-(1-hexylheptyl)-2-benzopyrano[6′,5′,4′:10,5,6]anthra[2,1,9-*def*]-isoquinoline-1,3,8,10-tetraone (**2**; 100 mg, 175 μmol). The mixture was stirred at 230 °C for 1 h, cooled, treated with $CHCl_3$, and poured into 2 M aqueous HCl (100 mL) with stirring. The organic phase was collected, washed with distilled water (2 × 50 mL) and with saturated aqueous NaCl (brine), dried with $MgSO_4$, and evaporated. The residue was purified by column separation (silica gel 800 × 44 mm, isohexane/chloroform 1/4). Yield: 65 mg (54%), red solid, Mp: >250 °C. $R_f$ value (silica gel, isohexane/$CHCl_3$ 1/4): 0.50. IR (ATR): $\nu$ 2914.8 (m), 2850.9 (w), 1693.2 (s), 1653.1 (s), 1593.5 (m), 1576.3 (w), 1503.8 (w), 1483.2 (w), 1454.7 (w), 1432.1 (w), 1404.8 (m), 1375.1 (w), 1332.2 (s), 1303.0 (m), 1281.3 (w), 1246.9 (m), 1203.9 (w), 1174.5 (w), 1163.1 (m), 1123.8 (w), 1104.0 (w), 1049.0 (w), 981.8 (w), 848.8 (m), 808.1 (s), 763.8 (w), 750.7 (m), 728.0 $cm^{-1}$ (m). $^1H$ NMR (600 MHz, $CDCl_3$, 25 °C): $\delta$ 0.82 (t, $^3J$(H,H) = 7.0 Hz, 6 H, 2 × $CH_3$), 1.19−1.38 (m, 16 H, 8 × $CH_2$), 1.73 (d, $^2J$(H,H) = 12.1 Hz, 3 H, 3 × $CH_{adamantane}$), 1.84−1.91 (m, 5 H, $\beta$-$CH_2$, 3 × $CH_{adamantane}$), 2.22−2.29 (m, 5 H, $\beta$-$CH_2$, 3 × $CH_{adamantane}$), 2.65 (d, $^3J$(H,H) = 2.7 Hz, 6 H, 3 × $CH_{2\ adamantane}$), 5.15−5.20 (m, 1 H, N-CH), 8.31−8.63 ppm (m, 8 H, 8 × $CH_{perylene}$). $^{13}C$ NMR (150 MHz, $CDCl_3$, 25 °C): $\delta$ 14.0, 22.6, 27.0, 29.2, 30.6, 31.8, 32.4, 36.5, 40.1, 54.8, 65.0, 122.4, 122.9, 125.7, 126.0, 126.3, 129.5, 130.0, 133.4, 165.1 ppm. UV/vis ($CHCl_3$): $\lambda_{max}$ ($\varepsilon$) 457.0 (18 000), 487.6 (48 800), 523.8 nm (79 000). Fluorescence ($CHCl_3$, $\lambda_{exc}$ 488 nm): $\lambda_{max}$ ($I_{rel}$) 532.8 (1.00), 575.4 (0.52), 622.5 nm (0.12). Fluorescence quantum yield ($CHCl_3$, $\lambda_{exc}$ = 488 nm, $E_{488\ nm/1\ cm}$ = 0.0143, reference **1a** with Φ = 1.00): 1.00. MS (DEP/EI): *m*/*z* (%) 707.6 (43), 706.6 (100) [$M^+$],

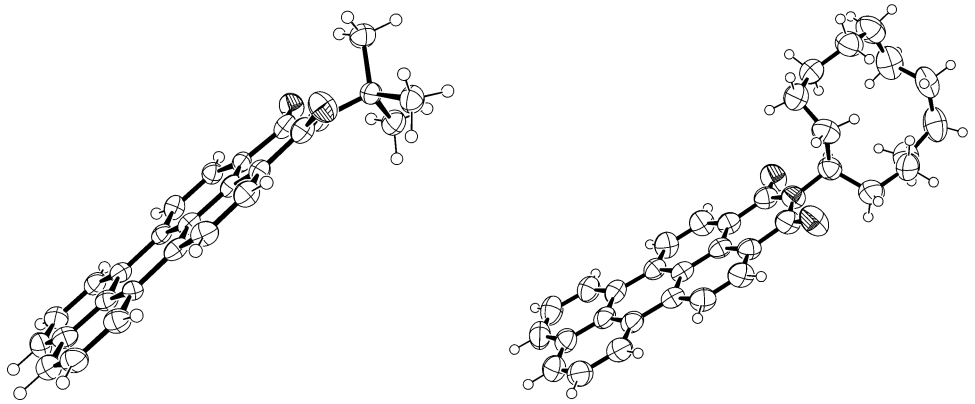
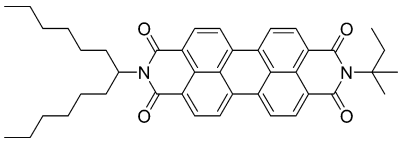


**Figure 5.** X-ray crystal structure analysis of **3a** (left) in comparison with the known crystal structure of *N*-cyclooctylperylene-3,4-dicarboxylic imide (right).


dx.doi.org/10.1021/jo300540h | J. Org. Chem. 2012, 77, 5965−5970

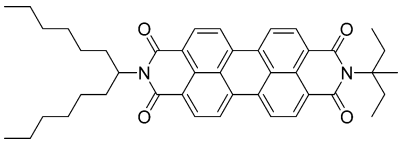
524.2 (30), 390.1 (24). HRMS ($C_{47}H_{50}N_2O_4$): calcd 706.3771 [$M^+$], found 706.3783 [$M^+$], Δ = +0.0012. Anal. Calcd for $C_{47}H_{50}N_2O_4$ (706.9): C, 79.85; H, 7.13; N, 3.96. Found: C, 79.89; H, 7.15; N, 3.86.

**2-*tert*-Pentyl-9-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (1d).** 9-(1-Hexylheptyl)-2-



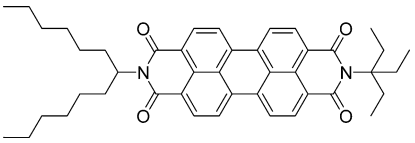
benzopyrano[6′,5′,4′:10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10-tetraone (**2**; 100 mg, 175 μmol) was dissolved in imidazole (179 mg, 2.63 mmol) at 150 °C and treated with *tert*-pentylamine (152 mg, 1.75 mmol). The mixture was kept at 150 °C for 30 min, cooled, treated with $CHCl_3$ (50 mL), washed with 2 M aqueous HCl (50 mL) and distilled water (2 × 50 mL), dried with $Na_2SO_4$, and evaporated in vacuo. The residue was purified by column separation (silica gel 800 × 44 mm, chloroform). Yield: 10 mg (9%), red solid. Mp: 230−231 °C. $R_f$ value (silica gel, chloroform): 0.45. IR (ATR): ν 2955.9 (w), 2922.8 (m), 2854.4 (w), 1695.7 (m), 1648.3 (s), 1594.4 (m), 1577.4 (m), 1505.5 (w), 1482.6 (w), 1459.6 (m), 1434.7 (w), 1405.9 (m), 1363.9 (w), 1332.1 (s), 1295.3 (w), 1249.1 (m), 1205.3 (w), 1163.9 (m), 1122.0 (m), 1109.4 (w), 1063.6 (w), 1008.7 (w), 959.4 (w), 853.1 (m), 808.1 (s), 764.1 (w), 740.0 $cm^{-1}$ (m). $^1H$ NMR (600 MHz, $CDCl_3$, 25 °C): δ 0.81 (t, $^3J(H,H)$ = 7.0 Hz, 6 H, 2 × $CH_3$), 0.88 (t, $^3J(H,H)$ = 7.1 Hz, 3 H, $CH_3$), 1.17−1.37 (m, 16 H, 8 × $CH_2$), 1.79 (s, 6 H, 2 × $CH_3$), 1.82−1.89 (m, 2 H, β-$CH_2$), 2.21−2.30 (m, 4 H, β-$CH_2$, $CH_2$), 5.14−5.20 (m, 1 H, N-CH), 8.46−8.68 ppm (m, 8 H, 8 × $CH_{perylene}$). $^{13}C$ NMR (150 MHz, $CDCl_3$, 25 °C): δ 9.0, 14.0, 22.6, 26.9, 28.2, 29.2, 31.7, 32.4, 33.9, 54.7, 65.1, 122.7, 123.0, 125.7, 126.1, 126.5, 128.7, 129.6, 130.3, 131.1, 131.8, 133.8, 134.6, 165.3 ppm. UV/vis ($CHCl_3$): $\lambda_{max}$ (ε) 456.2 (17 800), 487.0 (48 900), 523.2 nm (79 800). Fluorescence ($CHCl_3$, $\lambda_{exc}$ 487 nm): $\lambda_{max}$ ($I_{rel}$) 531.2 (1.00), 574.3 (0.51), 620.4 nm (0.12). Fluorescence quantum yield ($CHCl_3$, $\lambda_{exc}$ = 487 nm, $E_{487\ nm/1\ cm}$ = 0.0097, reference **1a** with Φ = 1.00): 1.00. MS (FAB$^-$): *m*/*z* (%) 642.3 (100) [$M^-$], 572.2 (21), 459.1 (25), 306.1 (80). HRMS ($C_{42}H_{46}N_2O_4$): calcd 642.3458 [$M^-$], found 642.3461 [$M^-$], Δ = +0.0003. Anal. Calcd for $C_{42}H_{46}N_2O_4$ (642.4): C, 78.47; H, 7.21; N, 4.36. Found: C, 78.19; H, 7.20; N, 4.28.

**2-(1-Ethyl-1-methylpropyl)-9-(1-hexylheptyl)anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (1e).** 9-(1-



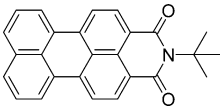
Hexylheptyl)-2-benzopyrano[6′,5′,4′:10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10-tetraone (**2**; 100 mg, 175 μmol) was dissolved in imidazole (179 mg, 2.63 mmol) at 150 °C and treated with 1-ethyl-1-methylpropylamine (178 mg, 1.75 mmol). The mixture was left at 150 °C for 20 min, cooled, treated with $CHCl_3$ (50 mL), washed with 2 M aqueous HCl (50 mL) and distilled water (2 × 50 mL), dried with $Na_2SO_4$, and evaporated in vacuo. The residue was purified by column separation (silica gel 800 × 44 mm, chloroform). Yield: 5 mg (5%), red solid. Mp: 210−212 °C. $R_f$ value (silica gel, chloroform): 0.55. IR (ATR): ν 2955.8 (w), 2925.9 (m), 2856.3 (w), 1695.0 (m), 1648.1 (s), 1595.7 (m), 1577.8 (w), 1505.1 (w), 1456.1 (w), 1433.9 (w), 1405.8 (m), 1386.4 (w), 1339.7 (s), 1329.4 (s), 1249.5 (m), 1206.4 (w), 1177.4 (w), 1163.9 (m), 1145.0 (w), 1124.9 (w), 1110.3 (w), 1057.9 (w), 964.1 (w), 852.7 (m), 809.4 (s), 751.3 (m), 730.4 (m), 654.8 $cm^{-1}$ (w). $^1H$ NMR (600 MHz, $CDCl_3$, 25 °C): δ 0.81 (t, $^3J(H,H)$ = 7.1 Hz, 6 H, 2 × $CH_3$), 0.91 (t, $^3J(H,H)$ = 7.4 Hz, 6 H, 2 × $CH_3$), 1.17−1.36 (m, 16 H, 8 × $CH_2$), 1.74−1.88 (m, 7 H, $CH_3$, 2 × β-$CH_2$), 2.19−2.27 (m, 2 H, β-$CH_2$), 2.69−2.77 (m, 2 H, β-$CH_2$), 5.14−5.20 (m, 1 H, N-CH), 8.51−8.71 ppm (m, 8 H, 8 × $CH_{perylene}$). $^{13}C$ NMR (150 MHz, $CDCl_3$, 25 °C): δ 8.9, 14.0, 22.6, 25.9, 26.9, 29.2, 31.7, 32.4, 32.6, 54.7, 68.9, 122.7, 123.1, 125.6, 126.2, 126.6, 128.9, 129.7, 130.5, 133.9, 134.7, 165.5 ppm. UV/vis ($CHCl_3$): $\lambda_{max}$ ($E_{rel}$) 456.8 (0.26), 487.4 (0.63), 523.8 nm (1.00). Fluorescence ($CHCl_3$, $\lambda_{exc}$ 487 nm): $\lambda_{max}$ ($I_{rel}$) 532.2 (1.00), 575.6 (0.51), 625.1 nm (0.12). Fluorescence quantum yield ($CHCl_3$ $\lambda_{exc}$ 487 nm, $E_{487\ nm/1\ cm}$ = 0.0143, reference **1a** with Φ = 1.00): 1.00. MS (DEP/EI): *m*/*z* (%) 656.4 (2) [$M^+$], 627.3 (2), 572.1 (24), 390.1 (100), 373.1 (7), 345.1 (9). HRMS ($C_{43}H_{48}N_2O_4$): calcd 656.3608 [$M^+$], found 656.3592 [$M^+$], Δ = −0.0016.

**2-(1,1-Diethylpropyl)-9-(1-hexylheptyl)-anthra[2,1,9-*def*;6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (1f).** 9-(1-



Hexylheptyl)-2-benzopyrano[6′,5′,4′:10,5,6]anthra[2,1,9-*def*]-isoquinoline-1,3,8,10-tetraone (**2**; 200 mg, 350 μmol) was dissolved in imidazole (179 mg, 2.63 mmol) at 150 °C and treated with 1,1-diethylpropylamine (402 mg, 3.50 mmol). The mixture was kept at 150 °C for 30 min, treated with $CHCl_3$ (100 mL), washed with 2 M aqueous HCl (100 mL) and distilled water (2 × 50 mL), dried with $Na_2SO_4$, and evaporated in vacuo. The residue was purified by column separation (silica gel 800 × 44 mm, chloroform). Yield: 4 mg (2%), red solid. Mp: 191−193 °C. $R_f$ value (silica gel, chloroform): 0.50. IR (ATR): ν 2954.6 (w), 2924.5 (m), 2855.3 (w), 1695.5 (s), 1650.9 (s), 1594.6 (m), 1577.6 (m), 1505.1 (w), 1458.0 (m), 1406.0 (m), 1324.4 (s), 1247.3 (m), 1203.5 (w), 1162.9 (w), 1139.0 (w), 1118.3 (w), 1067.7 (w), 961.5 (w), 921.4 (w), 850.9 (m), 809.3 (s), 748.0 (m), 724.0 (w), 701.6 $cm^{-1}$ (w). $^1H$ NMR (600 MHz, $CDCl_3$, 25 °C): δ 0.81 (t, $^3J(H,H)$ = 7.0 Hz, 6 H, 2 × $CH_3$), 0.91 (t, $^3J(H,H)$ = 7.2 Hz, 9 H, 3 × $CH_3$), 1.67−1.36 (m, 16 H, 8 × $CH_2$), 1.81−1.88 (m, 2 H, β-$CH_2$), 2.19−2.27 (m, 2 H, β-$CH_2$), 2.31 (q, $^3J(H,H)$ = 7.6 Hz, 6 H, 3 × $CH_2$), 5.14−5.20 (m, 1 H, N-CH), 8.51−8.70 ppm (m, 8 H, 8 × $CH_{perylene}$). $^{13}C$ NMR (150 MHz, $CDCl_3$, 25 °C): δ 9.3, 14.0, 22.6, 26.9, 28.1, 29.2, 31.7, 32.4, 54.7, 73.6, 122.7, 123.0, 123.1, 125.9, 126.2, 126.6, 128.9, 1297, 130.4, 130.4, 133.9, 166.0 ppm. UV/vis ($CHCl_3$): $\lambda_{max}$ ($E_{rel}$) 457.0 (0.22), 487.6 (0.61), 523.4 nm (1.00). Fluorescence ($CHCl_3$, $\lambda_{exc}$ 487 nm): $\lambda_{max}$ ($I_{rel}$) 531.0 (1.00), 573.7 (0.52), 621.6 nm (0.12). Fluorescence quantum yield ($CHCl_3$ $\lambda_{exc}$ 487 nm, $E_{487\ nm/1\ cm}$ = 0.0168, reference **1a** with Φ = 1.00): 1.00. MS (FAB$^-$): *m*/*z* (%) 670.3 (100) [$M^-$], 572.2 (23), 459.1 (12), 306.1 (60). HRMS ($C_{44}H_{50}N_2O_4$): calcd 670.3771 [$M^-$], found 670.3792 [$M^-$], Δ = +0.0021.

***N*-(*tert*-Butyl)perylene-3,4-dicarboximide (3a).** Perylene-3,4-dicarboxanhydride (50 mg, 0.16 mmol) was dissolved in imidazole



(110 mg, 1.6 mmol) at 150 °C and treated with *tert*-butylamine (120 mg, 1.6 mmol). The mixture was kept at 150 °C for 30 min, cooled, dispersed in a small amount of ethanol, and poured into 2 M aqueous HCl (50 mL). The precipitate was collected by vacuum filtration, dried at 110 °C, and purified by column separation (silica gel 800 × 44 mm, chloroform/ethanol 80/1). Yield: 3 mg (5%), red solid. Mp: >250 °C. $R_f$ value (silica gel, chloroform/ethanol 80/1): 0.50. IR (ATR): ν 2973.1 (w), 2919.4 (m), 2849.9 (w), 1920.3 (w), 1697.8 (m), 1649.7 (s), 1590.8 (m), 1569.0 (m), 1498.1 (w), 1481.4 (w), 1450.2 (w), 1428.3 (w), 1397.0 (w), 1370.3 (w), 1344.3 (m), 1315.9 (w), 1291.6 (w), 1257.8 (m), 1235.2 (w), 1204.6 (w), 1189.9 (w), 1164.9 (s), 1136.3 (w), 1121.9 (m), 1034.3 (m), 902.2 (w), 838.3 (w), 809.8 (s), 750.5 (m), 666.2 $cm^{-1}$ (w). $^1H$ NMR (600 MHz, $CDCl_3$, 25 °C): δ 1.83 (s, 9 H, 3 × $CH_3$), 7.59 (t, $^3J(H,H)$ = 7.8 Hz, 2 H, 2 × $CH_{perylene}$), 7.85 (d, $^3J(H,H)$ = 8.1 Hz, 2 H, 2 × $CH_{perylene}$), 8.34 (d, $^3J(H,H)$ = 8.0 Hz, 2 H, 2 × $CH_{perylene}$), 8.37 (d, $^3J(H,H)$ = 7.4 Hz, 2 H, 2 × $CH_{perylene}$), 8.42 ppm (d, $^3J(H,H)$ = 8.0 Hz, 2 H, 2 × $CH_{perylene}$). $^{13}C$


dx.doi.org/10.1021/jo300540h | J. Org. Chem. 2012, 77, 5965−5970

NMR (150 MHz, $CDCl_3$, 25 °C): $\delta$ 29.9, 61.3, 117.6, 120.1, 123.2, 123.6, 126.4, 126.9, 128.1, 129.4, 130.4, 130.5, 134.4, 136.2, 165.8 ppm. UV/vis ($CHCl_3$): $\lambda_{max}$ ($E_{rel}$) 474.8 (1.00), 497.8 nm (1.00). Fluorescence ($CHCl_3$, $\lambda_{exc}$ 475 nm): $\lambda_{max}$ ($I_{rel}$) 533.1 (1.00), 569.3 nm (0.83). Fluorescence quantum yield ($CHCl_3$ $\lambda_{exc}$ 475 nm, $E_{475\ nm/1\ cm}$ = 0.0276, reference **1a** with $\Phi$ = 1.00): 1.00. MS (DEP/EI): *m*/*z* (%) 377.1 (15) [$M^+$], 321.1 (100), 277.1 (11), 264.1 (7), 250.1 (8), 125.0 (4). HRMS ($C_{26}H_{19}NO_2$): calcd 377.1416 [$M^+$], found 377.1410 [$M^+$], $\Delta$ = −0.0006.

## ■ ASSOCIATED CONTENT

### Supporting Information

Tables, figures, and a CIF file giving crystallographic data for **3a**, spectroscopic data for **1a**−**f** and **3a**, and atomic coordinates of the calculated structures of **1h**−**j**, **3a**, and the simplified **1c** (*N*-1-adamantyl-*N*-isopropylperylene-3,4:9,10-tetracarboxbisimide). This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Financial support by the Fonds der Chemischen Industrie and the CIPSM cluster Munich Center for Integrated Protein Science is gratefully acknowledged.

## ■ REFERENCES

(1) See for example: (a) Smith, M. B.; March, J. *March's Advanced Organic Chemistry. Reactions, Mechanisms, and Structure*; Wiley: Hoboken, NJ, 2007, ISBN: 978-0-471-72091-1. (b) Chapman, N. B., Shorter, J., Eds. *Correlation Analysis in Chemistry*; Plenum Press: New York, 1978; ISBN 0-306-31068-6.

(2) Reviews: (a) Langhals, H. *Helv. Chim. Acta* **2005**, *88*, 1309−1343. (b) Langhals, H. *Heterocycles* **1995**, *40*, 477−500. (c) Langhals, H. Molecular Devices. Chiral, Bichromophoric Silicones: Ordering Principles in Complex Molecules. In *Silicon Based Polymers*; Ganachaud, F., Boileau, S., Boury, B., Eds.; Springer: New York, 2008; pp 51−63, ISBN 978-1-4020-8527-7, e-ISBN 978-1-4020-8528-4.

(3) (a) Würthner, F. *Chem. Commun.* **2004**, 1564−1579. (b) Ilhan, F. D.; Tyson, S.; Stasko, D. J.; Kirschbaum, K.; Meador, M. A. *J. Am. Chem. Soc.* **2006**, *128*, 702−703. (c) Vajiravelu, S.; Ramunas, L.; Vidas, G. J.; Valentas, G.; Vygintas, J.; Valiyaveettil, S. *J. Mater. Chem.* **2009**, *19*, 4268−4275. (d) Fortage, J.; Séverac, M.; Houarner-Rassin, C.; Pellegrin, Y.; Blart, E.; Odobel, F. *J. Photochem. Photobiol. A: Chem.* **2008**, *197*, 156−169. (e) Lukas, A. S.; Zhao, Y.; Miller, S. E.; Wasielewski, M. R. *J. Phys. Chem. B* **2002**, *106*, 1299−1306. (f) Würthner, F.; Sautter, A.; Schmid, D.; Weber, P. J. A. *Chem. Eur. J.* **2001**, *7*, 894−902. (g) Ford, W. E.; Hiratsuka, H.; Kamat, P. V. *J. Phys. Chem.* **1989**, *93*, 6692−6696. (h) Zhan, X.; Facchetti, A.; Barlow, S.; Marks, T. J.; Ratner, M. A.; Wasielewski, M. R.; Marder, S. R. *Materials* **2011**, *23*, 268−284. (i) Soh, N.; Ueda, T. *Talanta* **2011**, *85*, 1233−1237. (j) Usta, H.; Facchetti, A.; Marks, T. J. *Acc. Chem. Res.* **2011**, *44*, 501−510. (k) Metzger, R. M. *Anal. Chim. Acta* **2006**, *568*, 146−155. (l) Greene, M. *Performance Pigm.* **2002**, 249−261.

(4) Langhals, H. Description of properties of binary solvent mixtures. In *Similarity Models in Organic Chemistry, Biochemistry and Related Fields*; Zalewski, R. I., Krygowski, T. M., Shorter, J., Eds.; Elsevier: Amsterdam, 1991; Studies in Organic Chemistry *42*, pp 283−342, ISBN 0-444-88161-1.

(5) Langhals, H.; Demmig, S.; Huber, H. *Spectrochim. Acta* **1988**, *44A*, 1189−1193.

(6) (a) Langhals, H.; Demmig, S.; Potrawa, T. *J. Prakt. Chem.* **1991**, *333*, 733−748. (b) Demmig, S.; Langhals, H. *Chem. Ber.* **1988**, *121*, 225−230.

(7) Rademacher, A.; Märkle, S.; Langhals, H. *Chem. Ber.* **1982**, *115*, 2927−2934.

(8) Nagao, Y.; Naito, T.; Abe, Y.; Misono, T. *Dyes Pigm.* **1996**, *32*, 71−83.

(9) (a) Grimme, S.; Schreiner, P. R. *Angew. Chem.* **2011**, *123*, 12849−12853; *Angew. Chem., Int. Ed.* **2011**, *50*, 12639−12642. (b) Bondi, A. *Phys. Chem.* **1964**, *68*, 441−451.

(10) Feiler, L.; Langhals, H.; Polborn, K. *Liebigs Ann. Chem.* **1995**, 1229−1244.